



Comment on “Unraveling the role of cobalt in the direct conversion of CO₂ to high-yield liquid fuels and lube base oil” by Jo et al. [Appl. Catal., B 2022, 305, 121041]

ARTICLE INFO

Keywords

CO₂
Hydrogenation
Operando
IR
DRIFTS

ABSTRACT

The IR work reported in the paper by Jo et al. is critically re-analyzed and different interpretations are proposed, that invalidate some of the conclusions proposed by the authors.

A recent paper in this journal reported on the catalytic activity of cobalt-based catalysts used for the hydrogenation of CO₂ into higher hydrocarbons [1]. Interesting selectivities to C₅₊ and C₂₁₊ were obtained at high CO₂ conversion. *In situ* diffused reflectance FT-IR spectroscopy (DRIFTS) was used at high temperatures and pressures for cobalt reduction in H₂ (350 °C and 30 bars) and to monitor CO₂ + H₂ reaction (up to 270 °C and 40 bars). The authors concluded, partly based on these *in situ* DRIFTS data, that various oxidic and metallic phases of cobalt were present and that formates were possibly involved in the reaction mechanism. Unfortunately, several important flaws can be found in both the collection and the analysis of the DRIFTS data that invalidate the corresponding conclusions.

First and most significant, the assignment of most IR bands is incorrect. Fig. 1 compares the DRIFTS bands assigned to surface species by Jo et al. [1] (Fig. 1. A) and the gas-phase spectra of CO₂ and H₂O recorded in a 2-m pathlength transmission IR gas-cell by us (Fig. 1. B). All the bands assigned to CO adsorbed on various cobalt species (Fig. 1. A.α) are actually those of CO₂(g) (Fig. 1.B.α). The (very) weak CO₂ bands next the main asymmetric stretching of ¹²C¹⁶O₂ at 2349 cm⁻¹ (with intensity saturated here), are due to energy transitions (notably between excited states that are more populated at high temperatures) of CO₂ isotopic variants (with ¹²C or ¹³C and ¹⁶O, ¹⁷O or ¹⁸O). The details of more than five hundreds CO₂ bands located between 400 and 10,000 cm⁻¹ have been tabulated by Rothman et al. [2–4]. The same conclusion can be drawn for the bands near 1000 cm⁻¹ assigned by Jo et al. [1] to various methoxy and carbonates species (Fig. 1.A.γ), which are again actually associated with CO₂(g) (Fig. 1.B.γ). Note that the sharp band at 949 cm⁻¹ superimposed on that of CO₂ is specifically that of gas-phase C₂H₄.

The numerous bands in the region 1800–1300 cm⁻¹ assigned by Jo et al. [1] to various adsorbates (Fig. 1.A.β) are actually those of the gas-phase rovibrational spectrum of water (Fig. 1.B.β) [5,6]. This is especially obvious because these roto-vibrational bands are very narrow, the full width at half height (FWHH) being about 9 cm⁻¹. In contrast, bands of truly adsorbed species are significantly larger, e.g. on ZrO₂ the FWHH of the band of adsorbed water [7] at 1640 cm⁻¹ is about 44 cm⁻¹ and that of formate [8] at 1575 cm⁻¹ is about 52 cm⁻¹.

Therefore, it appears that the current DRIFTS analysis reported by Jo et al. [1], cannot be used to support the presence of various cobalt carbonyls and other surface species (whether or not those are actually present), since these authors mostly monitored the gas-phase signals of CO₂ and water, which overwhelmed the signal of adsorbates.

A second concern arises from the experimental conditions used in a spectroscopic cell (High-Temperature High-Pressure reaction cell from Harrick) that is renowned to exhibit major temperature control issues [9,10]. The temperature of the top of the catalyst bed under Ar at atmospheric pressure was measured to be only 285 °C when that in the bed bulk was 350 °C [8]. The temperature of bed surfaces in most DRIFTS cells is typically lower than that expected (i) because the beds are heated underneath and (ii) because of the heat loss through the gas-mediated convective thermal contact between the bed and the cell dome, usually kept at room temperature. The temperature gradient is expected to be far greater if H₂ or He are used, because of the higher thermal conductivity of these gases. The pressure of 30 bars of pure H₂ used by Jo et al. [1] to reduce the cobalt catalyst at 350 °C would have led to a far lower temperature of the catalyst top layer, possibly preventing the reduction of cobalt oxides. This would explain the apparent lack of Co⁰ carbonyl bands, that normally gives major IR signals in the 2060–1900 cm⁻¹ region [11,12].

A third concern is the use of a highly KBr-diluted catalyst sample, using proportions 5:95. This would inevitably lead to a low signal coming from the catalyst and, especially, likely give rise to chemical or structural modifications of the sample by KBr, as already reported by Bianchi and co-workers [13].

In conclusion, we believe that the DRIFTS data reported in the paper by Jo et al. [1] should be wholly reconsidered in view of the above-comments. We hope that these comments will provide a useful source of information to those using *in situ* and *operando* DRIFTS spectroscopy to investigate catalytic reactions, which is clearly not straightforward both on the experimental and data interpretation aspects, as discussed elsewhere [7,14].

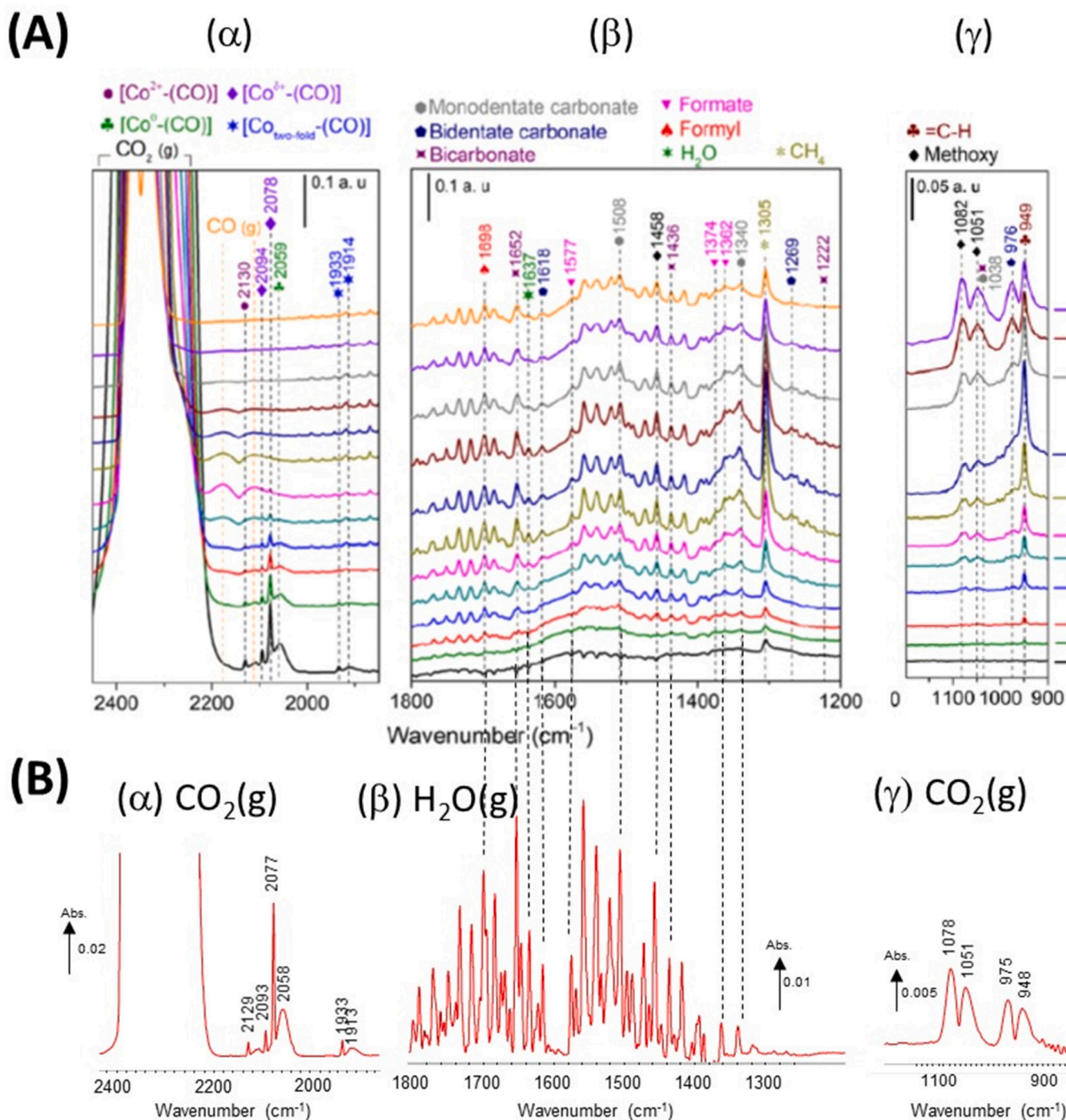


Fig. 1. Comparison of (A) in situ DRIFTS spectra reported in Fig. 5 by Jo et al. in ref. [1] and (B) corresponding regions showing the IR gas-phase spectra of pure CO₂ and H₂O/He collected by the present authors at 80 °C in a 2-m-long IR gas-cell.

Declaration of Competing Interest

There are no conflicts of interest to declare.

References

- [1] H. Jo, M.K. Khan, M. Irshad, M.W. Arshad, S.K. Kim, J. Kim, Unraveling the role of cobalt in the direct conversion of CO₂ to high-yield liquid fuels and lube base oil, *Appl. Catal. B Environ.* 305 (2022), 121041.
- [2] L.S. Rothman, L.D.G. Young, Infrared energy levels and intensities of carbon dioxide—II, *J. Quant. Spectrosc. Radiat. Transf.* 25 (1981) 505–524.
- [3] L.S. Rothman, Infrared energy levels and intensities of carbon dioxide. Part 3, *Appl. Opt.* 25 (1986) 1795–1816.
- [4] L.S. Rothman, R.L. Hawkins, R.B. Wattson, R.R. Gamache, Energy levels, intensities, and linewidths of atmospheric carbon dioxide bands, *J. Quant. Spectrosc. Radiat. Transf.* 48 (1992) 537–566.
- [5] F.C. Meunier, W. Li, Comment on the “In situ IR studies on the mechanism of methanol synthesis from CO/H₂ and CO₂/H₂ over Cu-ZnO-Al₂O₃ catalyst” by Wang et al, *Korean J. Chem. Eng.* 28 (2011) 1495–1496.
- [6] (<https://webbook.nist.gov/cgi/cbook.cgi?ID=C7732185&Units=SI&Type=IR-SPEC&Index=0#IR-SPEC>).
- [7] F.C. Meunier, R. Kdhir, N. Potrzebowska, N. Perret, M. Besson, Unravelling platinum-zirconia interfacial sites using CO adsorption, *Inorg. Chem.* 58 (2019) 8021–8029.
- [8] F.C. Meunier, I. Dansette, K. Eng, Y. Schuurman, Differentiating the reactivity of ZrO₂-bound formates formed on Cu/ZrO₂ during CO₂ hydrogenation, *Catalysts* 12 (2022) 793.

- [9] F.C. Meunier, Pitfalls and benefits of in situ and operando diffuse reflectance FT-IR spectroscopy (DRIFTS) applied to catalytic reactions, *React. Chem. Eng.* 1 (2016) 134–141.
- [10] H. Li, M. Rivallan, F. Thibault-Starzyk, A. Travers, F.C. Meunier, Effective bulk and surface temperatures of the catalyst bed of FT-IR cells used for in situ and operando studies, *Phys. Chem. Chem. Phys.* 15 (2013) 7321–7327.
- [11] A. Paredes-Nunez, D. Lorito, N. Guilhaume, C. Mirodatos, Y. Schuurman, F. C. Meunier, Nature and reactivity of the surface species observed over a supported cobalt catalyst under CO/H₂ mixtures, *Catal. Today* 242 (2015) 178–183.
- [12] A. Paredes-Nunez, D. Lorito, L. Burel, D. Motta-Meira, G. Agostini, N. Guilhaume, Y. Schuurman, F. Meunier, CO hydrogenation on cobalt-based catalysts: tin poisoning unravels CO in hollow sites as a main surface intermediate, *Angew. Chem. Int. Ed.* 57 (2018) 547–550.
- [13] J. Couble, P. Gravejat, F. Gaillard, D. Bianchi, Quantitative analysis of infrared spectra of adsorbed species using transmission and diffuse reflectance modes, *Appl. Catal. A Gen.* 371 (2009) 99–107.
- [14] F.C. Meunier, Relevance of IR spectroscopy of adsorbed CO for the characterization of heterogeneous catalysts containing isolated atoms, *J. Phys. Chem. C* 125 (2021) 21810–21823.

Frederic C. Meunier^{a,*}, Canio Scarfiello^b

^a Univ Lyon, Université Claude Bernard Lyon, CNRS, IRCELYON, 2 Av. Albert Einstein, 69626 Villeurbanne, France

^b Université de Toulouse, IMT Mines Albi, UMR CNRS 5302, Centre RAPSODEE, Campus Jarlard, 81013 Albi Cedex 09, France

* Corresponding author.

E-mail address: fcm@ircelyon.univ-lyon1.fr (F.C. Meunier).